

THE CHEMICAL EFFECTS OF NEUTRON AND
GAMMA IRRADIATION OF PHOSPHORUS
TRICHLORIDE

by

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B. S., Kansas State College of
Agriculture and Applied Science, 1956

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

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INTRODUCTION

Several nuclear transformations are induced when PCl_3 is irradiated with thermal neutrons. If the thermal neutron source is a nuclear reactor, the PCl_3 sample is also subjected to gamma radiation. Both the gamma rays and the nuclear reactions initiated by the neutrons are capable of supplying energy for promoting chemical reactions which would normally occur only at very high temperatures. The PCl_3 system is favorable for studying the chemical effects produced by these nuclear particles.

The average energy of the gamma rays in the Oak Ridge x - 10 graphite reactor has been estimated at 1 Mev (Collins and Calkins, 14). At this photon energy few nuclear reactions are initiated by gamma-ray absorption. Therefore, the important nuclear reactions are those produced by the neutrons.

Naturally occurring phosphorus is 100 per cent P^{31} while naturally occurring chlorine consists of 75.4 per cent Cl^{35} and 24.6 per cent Cl^{37} . When irradiated with thermal neutrons, these isotopes undergo the following nuclear reactions: $\text{P}^{31}(\text{n}, \text{r})\text{P}^{32}$, $\text{Cl}^{35}(\text{n}, \text{r})\text{Cl}^{36}$, $\text{Cl}^{37}(\text{n}, \text{r})\text{Cl}^{38}$ and $\text{Cl}^{35}(\text{n}, \text{p})\text{S}^{35}$. The energies released by these reactions were 7.94 Mev, 8.56 Mev, 6.11 Mev and 0.67 Mev respectively. This energy is divided between the recoiling nucleus and the departing particle. Often the recoiling nucleus¹ is given enough momentum to break one or more of the chemical bonds holding that atom in a molecule. For example the average recoil energy of P^{32} is about 170 ev². Since

¹Since energies greater than 2 ev are required to break most chemical bonds, the impact of thermal neutrons having a kinetic energy of 0.025 ev cannot cause bond rupture.

²Methods of calculating recoil energies are discussed in the literature review section.

the phosphorus-chlorine bond energy is 2.75 ev, (Pauling, 40) this recoil energy is more than sufficient to break one or more of the phosphorus-chlorine bonds.

Immediately after acquiring this energy the atom or molecular fragment is moving with a high velocity. This energy is soon dissipated through interactions with other molecules. During this process the fragment recombines into some chemical species.

Compared to the total number of atoms present, the number of nuclear reactions occurring in the sample is small. For example in one ml of PCl_3 only 1.3×10^8 atoms of P^{32} are produced in one second at a neutron flux of 1×10^{11} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. In order to follow the chemical effects of such a small number of nuclear reactions, the resulting nuclei must be radioactive. In addition, no exchange reactions can take place between the radioactive atoms and the solvent or the chemical identity of the species formed in the recoil process is lost. The different chemical species formed by the recoiling atoms are identified by adding carriers to the irradiated sample, performing separations, and then measuring the radioactivity present in the various separated carriers.

All nuclear reactions in the PCl_3 system produce radioactive nuclei which decay by beta emission. Cl^{38} has a short half life (37.5 minutes) and is completely decayed before sample analysis is begun. Cl^{36} has a long half life, 10^6 years, and is not detectable in such minute amounts. Both S^{35} and P^{32} have detectable activities, with maximum energies of .167 Mev and 1.7 Mev respectively. By the use of absorber counting techniques the individual activities may be traced. In the present study only the P^{32} activity was followed due to counting equipment limitations.

The energy imparted to the sample by the recoiling atoms produced from

radiative neutron capture is actually a small fraction of the total energy absorbed by the sample. The other sources of energy are:

1. Attenuation of the gamma rays which are present in the reactor.
2. Attenuation of the gamma rays produced by the (n,γ) nuclear reactions within the sample.
3. Absorption of the kinetic energy of the protons produced by the $\text{Cl}^{35}(n,p)\text{S}^{35}$ reaction.
4. Attenuation of the fast neutrons in the reactor.

A large part of this absorbed energy is dissipated through ionization and excitation of PCl_3 molecules. These ionized and excited molecules or stable radiolysis products from them may react with the original chemical species produced by the $\text{P}^{31}(n,\gamma)\text{P}^{32}$ reaction to give different products containing P^{32} atoms. If such reactions do occur and if the rate of production of the radicals, excited molecules, or stable radiolysis products is different from the rate of production of recoil products, a distribution of the compounds containing P^{32} atoms as a function of irradiation time could be expected.

Purified PCl_3 samples were irradiated at the Oak Ridge National Laboratory for various lengths of time in order to experimentally test this theory. The influence of gamma radiation upon the recoil products was also studied by irradiating two samples for equal lengths of time in the nuclear reactor and then subjecting one to additional gamma dosage. Information concerning the magnitude of the gamma ray influence upon the system was obtained from a calculation of the energy deposited in the sample during irradiation in the reactor. The nature of the interaction between the gamma rays and PCl_3 was studied by irradiating a solution of white phosphorus, containing P^{32} , dissolved in PCl_3 with gamma rays from a ^{60}Co source. These data contributed towards understanding the mechanism of the recoil reactions and the effects resulting from the attenua-

tion of gamma rays, fast neutrons, etc.

LITERATURE REVIEW

An attempt has been made to survey the literature which pertains to the chemical effects accompanying radiative neutron capture. This survey does not cover the entire field; emphasis is placed upon the mechanism for energy transfer from the recoiling atom to the remainder of the system. In addition this survey includes other systems which may be helpful in understanding the FeCl_3 problem.

Recombination Mechanisms

According to Maddock, the recoil atoms from radiative neutron capture, (n, γ) reactions, may attain a translational energy of several electron volts. The temperature necessary to produce such energies is some tens of thousands of degrees. By the application of conservation of energy and momentum principles, the energy of the recoiling atom, E_R , is shown to equal $536(E_\gamma)^2 / M \text{ ev}$ where E is the gamma-ray energy in Mev and M is the mass of the atom in atomic mass units. The derivation of this equation can be found in nearly all radiochemistry books. The equation is derived by equating the momentum of the photon to that of the recoiling atom; therefore, if more than a single gamma ray is emitted the above equation cannot be applied. Kinsey et al. (30) found that the gamma-ray spectra associated with the capture of neutrons is complex. This results in a range of recoil energies. For example Wahl and Bonner (50) showed that if two gamma rays of energy E_1 and E_2 are emitted in cascade, the final recoil energy lies between the limits $536(E_1 + E_2)^2 / M \text{ ev}$ and $536(E_1 - E_2)^2 / M \text{ ev}$.

Muehlhause (38) found that the average number of gamma rays emitted for

light nuclei was 2.5 per neutron capture. There was no evidence for an angular distribution of emitted gamma rays or an effect due to the energy of the neutron for low energy neutrons. He measured an average of 3.1 gamma rays per neutron capture for chlorine. Kinsey et al. (30) investigated the gamma-ray spectrum of phosphorus, sulfur, chlorine, potassium, and calcium. Their data support those of Muehlhause on chlorine. In the $P^{31}(n,\gamma)P^{32}$ reaction, the P^{32} nucleus loses 7.94 Mev in returning to the ground state. Kinsey et al. showed an energy level diagram for the P^{32} nucleus which indicates that the first gamma ray must have an energy greater than 3.5 Mev. The remaining energy is then dissipated in one or more gamma rays.

It is conceivable that the gamma rays could be emitted in opposite directions, giving the atom no momentum. Willard (52) stated that if the time between emission of consecutive gamma rays is greater than the time required for an atom to move about one atomic diameter, about 10^{-14} seconds, the atom may break its bond as a result of the separate recoil impulses even where complete cancellation of energy would have occurred from simultaneous gamma emission. According to Bethe (4), the lifetimes of the nuclei in the cascade process probably vary from 10^{-17} seconds to longer than 10^{-14} seconds. Experimental results from neutron irradiation in the gaseous phase of ethyl bromide by Wexler and Davies (51), butyl chloride by Chien and Willard (9), trifluoromethane by Rice and Willard (42), and other data show that bond rupture accompanies over 99 per cent of the nuclear reactions. From this Willard (52) concluded that gamma-ray cancellation is relatively unimportant in preventing bond rupture. He also stated that it is impossible to calculate an average recoil energy with the available data. According to Maddock (35), more than 95 per cent of the recoil atoms receive enough energy to break a single bond; however, if the activated atom is held by two or more bonds there is a proba-

bility of not breaking all the bonds.

Most authors agree that nuclear transformations yield atoms with high electrical charge as well as high recoil energy. This electrical charge can produce chemical changes through molecular dissociations. This additional mechanism depends upon the creation of a highly charged positive ion through the interaction of the emitted particle and the orbital electrons of the disintegrating atom. Maddock (35) described this process and stated that the probability of ionization is high for the emission of heavy, charged particles, but low for gamma emission unless internal conversion occurs. Internal conversion of a K or L electron can produce a highly charged positive ion through Auger multiplication. Internal conversion also leads to greater mechanical recoil than the alternate photon emission because of the greater momentum of the electron. According to Willard (52) evidence for internal conversion has been found for all nuclei which have been studied; however, many have not been investigated. Wexler and Davies (51) found that 12 per cent of Br^{80m} , 25 per cent of Br^{82} , 50 per cent of I^{128} , and 18 per cent of Br^{80} were positively charged during the stabilization of the compound nucleus following neutron capture of ethyl bromide and ethyl iodide. In the isomeric transition, $\text{Br}^{80m} \rightarrow \text{Br}^{80}$, with the emission of a 0.09 Mev gamma ray, Wexler and Davies (51) measured the average charge on the Br^{80} as $\dagger 10$. Perlman and Minkel (41) measured the charge of Xe^{131m} in the $\text{Xe}^{131m} \rightarrow \text{Xe}^{131}$ reaction as $\dagger 8.5$.

According to Carlson and Koski (6) self-ionization by a rapidly moving particle is not probable unless the particle has a velocity comparable to the velocity of free electrons. Yossim and Davies (57) obtained data which indicated that the internal conversion process which produces the charge on silver and indium recoil atoms occurs after the emission of the energetic gamma rays.

Willard (52) concluded that the chemical effects following neutron capture result in part from the neutralization of the charge produced on the atom by internal conversion after it has lost its recoil energy.

Szilard and Chalmers (49) were the first investigators to separate recoil atoms from the irradiated target. Consequently such reactions are often called Szilard-Chalmers reactions. They irradiated ethyl iodide with thermal neutrons and recovered a large fraction of the radioactive iodine as free iodine. Since this experiment in 1934, many alkyl halides have been investigated. The distribution of the radioactive halogen, that is whether the recoil products are organic or inorganic compounds, depends to a great extent upon whether the irradiations are done in the gaseous or liquid state. Wahl and Bonner (50) stated that in the liquid phase about 50 per cent of the radioactive halogen is recombined with organic molecules, while in the gaseous phase very little radioactive halogen is recombined into organic molecules. Attempts to explain the reactions of the alkyl halides in the liquid phase have resulted in two theories, the "billiard ball, epithermal collision" hypothesis and the "random fragmentation" hypothesis. The theories have since been extended to other systems in addition to the alkyl halides.

Libby (34) proposed the "billiard ball hypothesis" in 1947. This theory assumed that the recoiling atom loses little of its energy by ionization of surrounding molecules. The ionization mechanism requires successive electron captures and ejections by the recoil atom. Since most recoil atoms have velocities below that of free electrons, they cannot undergo self ionization. Therefore, the assumption that the recoil atom will not lose energy by ionization should be valid. The postulated energy transfer mechanism consists of collisions between the recoil atom and the other atoms in the system. It is assum-

ed that the energy or momentum transfer occurs just as if the atoms were in the gas phase, or in other words the collisions are assumed to be elastic. The fractional energy loss per collision, $\Delta E/E$, is given by the following equation:

$$\frac{\Delta E}{E} = \frac{2MM_1 - 2M_1M \cos \theta}{(M + M_1)^2}$$

where M and M_1 are the masses of the struck and impinging atom respectively, and θ is the angle between the original and final paths of the impinging atom. The greatest energy transfer occurs when M equals M_1 which results in complete transfer for head on collisions, i. e. $\theta = 180^\circ$.

In the "billiard ball" collision theory the collisions between atoms of nearly equal mass account for the chemical reactions which occur while the recoil atom still has energy in excess of 10 ev (hot reactions). For example, consider a collision between M and M_1 where both have nearly equal masses. Much of the recoil energy from M_1 will be transferred to M ; therefore, M may break its bonds and leave the immediate vicinity. The radicals resulting from the bond breakage and M_1 , held together by the solvent cage until they are thermalized, combine to form a stable molecule. The lack of the solvent cage in the gas phase irradiation explains the low per cent of radioactive halogen present in organic molecules. When no cage is present the radioactive halogen is not held close to the radicals, and it diffuses away to form inorganic compounds with hydrogen or inactive halogen. Many of the atoms, M_1 , will not undergo the hot reactions but will be cooled through successive collisions. Libby (34) stated that when the energy of the recoil atom has decreased until it approaches the bond energies of molecules, inelastic collisions with the molecules are prevalent. In these collisions the struck molecule is likely to acquire internal vibrational energy which may cause dissociation. If dissocia-

tion does occur, the recoiling atom M, and the resulting radicals held together by the solvent cage, may combine to form stable molecules. Friedman and Libby (22) called such reactions of the relatively cool recoil atom, epithermal reactions. They postulated these reactions to explain dibromo and other complicated organic products formed in the neutron irradiation of n-propyl bromide. They also pointed out the possibility for reactions between the solution and the recoil atoms which manage to enter the thermal energy range without chemical combination.

In his review of 1955 Willard (52) pointed out that the "billiard ball" hypothesis does not explain all the facts which are known about alkyl halide systems. He proposed the "random fragmentation" model which postulated that the rapidly moving atom encounters a solvent molecule before traveling a distance greater than a molecular diameter. If this were an isolated molecule, an elastic collision would occur, but in the liquid phase this cannot happen because the struck molecule is backed and surrounded by a close packed wall of other molecules. The result is a dissipation of energy by breaking of bonds in a rather indiscriminate fashion in the immediate vicinity of the energetic atom. The recoil atom may combine with these radicals which it has formed while it still has energy above thermal energies. Such reactions are called hot reactions and are characterized by temperature independence and insensitivity to added reagents which would inhibit the analogous thermal reactions. In addition to hot reactions Willard (52) proposed a process for recombination whereby the atoms reach thermal energies, diffuse through the system, and combine with radicals which they formed while losing their energy. According to Willard (52) the chemical characteristics of the solvent in which a recoil atom finds itself is one of the most important factors in determining its fate.

Physical factors such as recoil energy, charge, cage strength, mass of atoms, density, etc. probably play minor roles.

The "random fragmentation" theory predicts that many different kinds of products will be formed. This was verified by Evans and Willard (19) when they separated 20 different organic compounds containing radioactive bromine from a 30 minute neutron irradiation of n-propyl bromide.

At the present time much work is being done to differentiate between hot and thermal reactions in terms of the "random fragmentation" theory. Some progress is being made with the use of radical scavengers which will react with the recoiling atom as soon as it approaches thermal energies. Goldhaber and Willard (25), Levey and Willard (33), and Chien and Willard (9) have used free halogens as a scavenger in the alkyl halide series. Williams et al. (55) discovered that dibromoethylene will react with bromine atoms but not bromine molecules. A recent article on the irradiation of n-propyl bromide by Chien and Willard (7) illustrated typical results obtained in scavenger studies. Using bromine as the scavenger they found that the fraction of radioactive bromine that enters into organic combinations by hot processes and the fraction which enters after thermal diffusion is the same for $\text{Br}^{79}(n,\gamma)\text{Br}^{80}$ and $\text{Br}^{79}(n,\gamma)\text{Br}^{80m}$ reactions. The data indicate that the recombinations of the thermalized Br and the radicals formed from the rupture of C-Br and C-C bonds occur largely by diffusion. However, the recombination of radicals formed from breaking C-H bonds and the thermalized Br occurs immediately after thermalization rather than by reaction after the Br atom has diffused from its site of formation. In the same study on n-propyl bromide, they found that n-hexyl bromide and the 1 - 3 dibromopropane are formed almost exclusively by hot reactions.

Another method used to study recombination involves irradiating solutions of the material in chemically inert solvents. Aditya and Willard (1) list

several reasons why they studied the irradiation of alkyl halides dissolved in a series of hydrocarbons. Briefly they are:

1. The sizes and weights of the molecules which surround the activated halogen atom can be varied without changing the types of bonds to be broken.
2. From the conservation of energy requirements the halogen atom cannot undergo a hot "billiard ball" collision reaction.
3. Investigation can be made whether or not the size of the hydrocarbon molecules influences the organic yield of radioactive bromine.
4. The study should contribute towards a better understanding of the mechanisms of various hydrogen replacements by halogens.

Gavoret (23,24) and Ivanoff and Gavoret (29) investigated the (n,γ) activation of free halogens dissolved in substituted aromatic compounds. Ratios of the substitution products formed, including the ortho, meta, and para isomers are compared. From these data interpretations are made concerning the recoil atom's energy and charge when the substitution product was formed. For example, Gavoret (23) found that the relative rates of substitution of Br^{82} on the benzene ring in toluene, nitrobenzene, and acetophenone are 0.89, 0.26, 0.39 respectively where the substitution rate on benzene is considered as unity. The $-\text{CH}_3$, $-\text{NO}_2$, and $-\text{COCH}_3$ groups cause deactivation of the benzene ring towards electrophilic reagents. Furthermore the deactivation increases in the series $-\text{CH}_3$, $-\text{COCH}_3$, $-\text{NO}_2$. These data showed that the mechanism for substitution by Br^{82} cannot be explained using only the free radical combinations, but must be attributed partly to an ionic mechanism involving a positively charged bromine ion.

Both the "billiard ball" hypothesis and the "random fragmentation" hypothesis have been extended to the solid state. In general, neutron irradiation

of solid alkyl halides results in increased recombination of the radioactive halogen into organic molecules in comparison to liquid phase irradiations.

In the "billiard ball" hypothesis Fox and Libby (20), Friedman and Libby (22), Rowland and Libby (44) postulated that the recoil atom, through multiple collisions, melts a pear shaped volume in the solid which contains about 1000 molecules. In some cases the recoil atom will transfer its energy to another atom of about equal weight and enter into combinations while the energy is still high. Such combinations occur near the center of the melted volume and would be the same as those occurring in a liquid medium. After the atom has lost most of its recoil energy, it may rupture a molecule in an epithermal collision and combine with the resulting radicals. Such events will occur at the edge of the molten region where the cage wall will be much stronger than in the liquid medium. This stronger cage wall is supposed to enhance organic combinations.

Willard (52) questioned the last statement since Goldhaber and Willard (25) showed that inorganic and organic combinations occur in both the high energy and thermal regions. According to Willard (52) several things are important in the solid state irradiations. For example the probability of different type of bond rupture varies with the density and crystal structure. Also the difference in rates of diffusion of organic and inorganic radicals from the region of the cooled atoms may be important. In summary, Willard believes that the net results vary from compound to compound.

Most of the literature references pertain to (n,γ) or $(n,2n)$ nuclear reactions. Usually nuclear reactions involving the emission of charged particles give nuclei with higher recoil energies and greater charge. Willard (52) stated that the chemical effects should be the same whether reactions involve the emission of a charged particle or the emission of a gamma ray, providing both

recoiling nuclei have the same atomic number. Considerable data have been reported supporting this theory. Schuler (46) reported that the reactions $I^{127}(d,p)I^{128}$, $I^{127}(n,2n)I^{126}$ and $I^{127}(\gamma,n)I^{126}$ with recoil energies in excess of 100,000 ev gave the same organic yields of radioactive iodine as did the $I^{127}(n,\gamma)I^{128}$ reaction of much lower recoil energy. This work was done with alkyl iodides. Rowland and Libby (44), McCauley et al. (37), Schuler and McCauley (47), Evans and Willard (19), Chien and Willard (10 and 7) and other workers have found similar results for a variety of compounds and reactions. Schuler and McCauley (47) also reported that recoil atoms with a wide variation in energies may give different products in certain chemical environments.

To this author it appears that most investigators favor the "random fragmentation" model. However there is one notable exception. Rowland et al. (45), Hoff and Rowland (27) and Wolfgang et al. (56) have labeled glucose, galactose, ethane, methane, alcohols, and acetone with tritium by the $Li(n,\alpha)T$ reaction. They postulate that the final chemical combination for a large fraction of the combination occurs at low energies and involves only one tritium atom and one disrupted molecule. This is reasonable in view of the fact that many of the complex organic molecules were not broken up. Instead a high yield of undamaged labeled product was obtained, thus substantiating the "billiard ball, epithermal" theory. However, the recoiling tritium atom is small and should approach the billiard ball assumptions more closely than other recoiling atoms.

Conn (15) concludes that the "random fragmentation" theory gives a better description of the recoil processes than the "billiard ball collision" theory. However, he also points out that the "random fragmentation" theory is only a qualitative picture and a more quantitative description is needed. Maddock (35) stated that "although satisfactory interpretations of most of the effects have

been advanced, the satisfactory identification of the mechanisms involved cannot be expected until additional critical experiments have provided more accurate quantitative data."

Experimental Details

Great care must be exercised in the purification of compounds prior to irradiation with thermal neutrons. For example Friedman and Libby (22) reported the organic yield from the irradiation of *n*-propyl bromide as 50 per cent using samples which "were redistilled and their refractive indices found to check with those of the pure product within one part in ten thousand." Three years later the same laboratory, Fox and Libby (20), reported a 35 per cent yield if the same material was purified prior to irradiation by a treatment with ozone followed by distillation and washing. According to Willard (52) the impurity concentrations are so low that there is no certainty that any purification procedure will remove all impurities or not induce new ones. He stated that the most reliable criteria for purity is to obtain identical results from reagents purified by widely different methods.

Gamma Radiation Effects

When samples are subjected to thermal neutrons, they are also exposed to gamma rays and fast neutrons. These radiations produce ions, free radicals, and excited molecules.¹ Willard (52) stated that it is essential to know whether the fate of the activated atoms is altered by these radicals.

Levey and Willard (33) showed that the probability of interaction of the

¹Hereafter these products will be referred to as radicals.

hot² atoms with radicals is negligible. They base their argument upon the condition that the steady state concentration of radicals is 10^{-11} mole fraction at a radiation dosage of five thousand roentgens per hour while each thermalized recoil atom is present in a volume element containing self produced radicals at a mole fraction of 10^{-3} . Since the interaction of gamma rays with matter depends primarily upon the electron density, this condition should apply to all liquid systems. Even though the hot atom itself does not react with the radicals, the possibility of a reaction between the stable species containing the activated atom and the radicals still exists.

Chien and Willard (8) found that a wide variation of the gamma-ray intensity and total dosage during neutron irradiation of organic halides did not alter the product yields within the low dosage range used in most studies. However, when pure, degassed n-propyl bromide was irradiated for an hour at a flux of 10^{12} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ and a gamma-ray intensity of 10^6 roentgens per hour, the organic yield of $\text{Br}^{81}(n,\gamma)\text{Br}^{82}$ reaction was 90 per cent. In comparison, an organic yield of 32 per cent was observed at relatively low radiation intensities. They postulated that the gamma radiation produced "olefin like" species which were able to react with Br^{82} or HBr^{82} formed by the (n,γ) reaction to form organic materials. They showed that the "olefin like" impurities were not free radicals but stable materials. Applying this study to other systems, Chien and Willard state that in systems where radiolysis does not produce a stable substance which can react with the product from the (n,γ) reaction, no change in product yields would be expected as a result of increased gamma dosage. In another work with n-propyl bromide Chien and Willard (10) found that the

²The term, hot, describes the recoil atom before it has recombined into a stable molecule.

sample must receive about 10^5 roentgens before the organic yields increased.

Williams (54) irradiated SbF_5 and found that the per cent of radioactive antimony present as antimony pentafluoride increased with length of irradiation. For short periods of irradiation, about five minutes in a nuclear reactor, nearly 60 per cent of the activity was present as a non-volatile compound, presumably antimony trifluoride. After 26 hours of irradiation the per cent of the activity present in the non-volatile form dropped to 5 per cent of the total. Williams suggested that a back reaction converting SbF_3 into SbF_5 was induced by some component of the radiation field other than slow neutrons.

Cleary et al. (12) irradiated solid samples of alkali metal iodates with neutrons. They found that the absorption of heat or ionizing radiation after neutron bombardment produced an increase in the per cent of radioactive iodine present as the iodate ion.

Cobble and Boyd (13) investigated the effect of heat treatments and absorption of ionizing radiation upon the neutron irradiation of potassium bromate. They found that the per cent of radioactive bromine present as bromate at an extrapolated zero time was 9 per cent and increased to a limit of 32 per cent after 16 hours of irradiation. Heating the neutron irradiated potassium bromate sample above 80°C or exposing it to a Co^{60} gamma-ray source returned the radioactive bromine to bromate at a rate dependent upon the temperature and the intensity of the gamma radiation source. They explained the return of radioactive bromine to bromate as an exchange reaction between a trapped radioactive bromine atom and an adjacent bromate radical excited or ionized by gamma rays.

Systems Related to Phosphorus Trichloride

According to Wahl and Bonner (50) the various chemical forms of the recoil

atoms must not exchange during the irradiation and chemical separation if any value is to be obtained from following the tagged atoms. In the phosphorus trichloride system it is important to know whether or not the phosphorus can exchange with other phosphorus-chlorine compounds.

Using Cl_2^{38} , Koskoski and Fowler (32) found exchange between Cl_2^{38} and PCl_3 with less than 70 seconds half time for exchange, and exchange between Cl_2^{38} and PCl_5 with less than 40 seconds half time. Becker and Johnson (2) measured the exchange of phosphorus atoms between PCl_3 and PCl_5 in carbon tetrachloride. They interpret the observed exchange in terms of a first order decomposition: $\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$. Actually it is chlorine exchange rather than a phosphorus exchange. In the same work it was found that phosphorous acid and POCl_3 did not exchange.

Muxart et al. (39) studied the exchange between elemental phosphorus and PCl_3 in carbon disulfide solution. They found 4 per cent exchange in a few minutes and up to 30 per cent exchange in a few days. No mechanism was reported.

Working with P^{32} Conn and Hein (17) found that PCl_3 and elemental phosphorus do not exchange even when heated to 78°C for 75 hours or irradiated with a gamma dosage of 6×10^4 roentgens. This work was done with a heterogeneous system of red phosphorus and PCl_3 . They also found that P^{32} did not exchange between PCl_3 and PSCl_3 .

In 1937 Erbacher and Phillip (18) recovered an ionic form of phosphorus from a neutron irradiated triphenyl phosphate sample. Since that time, several phosphorus compounds have been irradiated with neutrons. Very little of this work contributes directly to an understanding of the phosphorus trichloride system. Those studies which are relevant are discussed below.

Carlson and Koski (6) found that x-rays and gamma rays had a large influ-

ence on the oxidation state of P^{32} which was produced by the $Cl^{35}(n,\alpha)P^{32}$ reaction in potassium chloride. The amount of pentavalent phosphorus increased with increasing gamma dosage. They postulated that the gamma radiation produced free chlorine which oxidized the phosphorus to the pentavalent state. They also irradiated a potassium chloride sample with 14 Mev neutrons. Under these conditions the recoiling phosphorus fragment has sufficient velocity to undergo self ionisation and three electrons may be lost. This sample had the least amount of pentavalent phosphorus indicating that recoil energy has little to do with the final oxidation state.

Phosphorus trichloride was irradiated by Hein and McFarland (26) for use in the synthesis of O, O, diethyl -O- p-nitrophenyl thiosulfate (parathion). They found only P^{32} and S^{35} activities present in the irradiated sample. Conn and Hein (17) did a more complete analysis of the PCl_3 system. They state, "from cross section and neutron energy considerations 98 to 99 per cent of the P^{32} atoms are formed by the $P^{31}(n,\gamma)P^{32}$ process and the remainder by the $Cl^{35}(n,\alpha)P^{32}$ process." They report that approximately 88 per cent of the total P^{32} atoms were either retained or reformed as the phosphorus trichloride molecule irrespective of total flux, temperatures or physical state (i.e. gas or liquid). The remaining P^{32} radioactivity was associated with unidentified compounds which have boiling points near and above $125^{\circ}C$. Assuming that the P^{32} atoms have enough energy to break all their original bonds, the high constant retention of the P^{32} atoms as phosphorus trichloride is difficult to understand on the basis of present theories. Although not completely satisfactory, Hein and Conn give a reasonable explanation of such a high per cent retention in the liquid phase using the "random fragmentation" theory. The high per cent of P^{32} radioactivity present as PCl_3 in the gas phase is not adequately

explained. They suggest that the system may be influenced by gamma dosage in a manner similar to SbF_5 causing incorporation of the P^{32} atoms back into PCl_3 .

EXPERIMENTAL PROCEDURE

The experimental procedure for studying the chemical changes produced in phosphorus trichloride by neutrons and gamma radiation can be broken into three steps. First, samples of purified PCl_3 are prepared. Second, the purified samples are irradiated, and third, the irradiated samples are analyzed for chemical changes.

Purification of the Phosphorus Trichloride Samples

Phosphorus trichloride was purified using the procedure developed by Gonn and Hein (17). Mallinckrodt reagent grade PCl_3 was quadruply distilled at atmospheric pressure through an eight inch glass, helix packed column. Only the middle fraction was collected during each distillation. The purified phosphorus trichloride was then distilled into a 19mm x 6.2 cm quartz ampoule under a reduced pressure of about 150 mm. Extreme care was taken to remove all traces of oxygen and water vapor from the vacuum distillation system before distillation. This was done by alternately evacuating and flushing the system several times with helium. The ampoule was connected to the vacuum distillation system by a small capillary tube and was filled from one-half to three-fourths full. During the distillation the ampoule was immersed in a dry ice and acetone bath. After collecting the desired amount of PCl_3 , the system was again flushed several times with helium. The pressure was reduced to 150 to 300 microns, the dry ice and acetone trap removed, and the ampoule sealed by

heating the capillary tube with a hot flame. This technique gave purified phosphorus trichloride in a sealed quartz container under an inert atmosphere of helium.

Irradiation of the Phosphorus Trichloride Samples

Two locations in the x -10 graphite reactor of the Oak Ridge National Laboratory were used for irradiations in this study. One location operates at a neutron flux of 1×10^{11} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ and a gamma flux of 5.6×10^4 roentgens hr^{-1} ; the other has a neutron flux of 6×10^{11} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ and a gamma flux of 1.55×10^6 roentgens hour^{-1} . Accurate measurement of the neutron dosage received by each sample was extremely important in this study. The actual neutron dosage was determined at Kansas State College by measuring the total P^{32} activity present in each sample. The method used for calculating the neutron dosage is shown in Appendix I. The relative probable error in the neutron dosage calculations was estimated as ± 5 per cent. Absolute dosage on the whole series may be in error by ± 15 per cent due to the uncertainty of the absolute geometry assigned to the detecting device and the uncertainty in the reported cross section value for phosphorus. From the neutron dosage the number of internally generated gamma rays from the (n, γ) reactions was estimated. The gamma dosage from external sources was obtained by multiplying the irradiation time by the reported gamma flux at that location in the reactor.

Analysis of the Irradiated Phosphorus Trichloride Samples

The PCl_3 samples were returned to the Kansas State College for analysis and always arrived within two days after irradiation. When opening the samples, precautions were taken to prevent hydrolysis or excessive loss due to evapora-

tion. The quartz ampoule and contents were first cooled in a dry ice and acetone bath. Next the tip of the ampoule was broken and its contents transferred to a 100 ml distillation flask which was surrounded with dry ice, thus producing a partial carbon dioxide atmosphere. Carriers were added to the distillation flask, standard counting samples were removed and then the solution was fractionally distilled.

The PCl_3 , POCl_3 , and PSCl_3 carriers used in this study were purified by repeated distillations. In the earlier studies reagent grade decane was used without treatment. In the later experiments the decane was purified by shaking with concentrated sulfuric acid for 10 to 12 hours, washing with water and then distilling.

The usual method for the addition of carriers and removal of standards¹ is shown in Fig. 1. The standards were used to determine the total P^{32} activity in

Dilution scheme for an irradiated sample

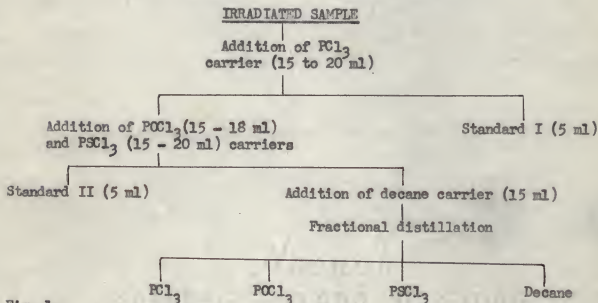


Fig. 1.

¹The term, standards, refers to the aliquots removed prior to the fractional distillation.

a sample. The first was removed following the addition of the PCl_3 carrier while the second was removed after the addition of POCl_3 and PSCl_3 . Large enough volumes were removed so that several counting samples could be prepared. Using two standards increased the reliability of the measurement of the total P^{32} activity.

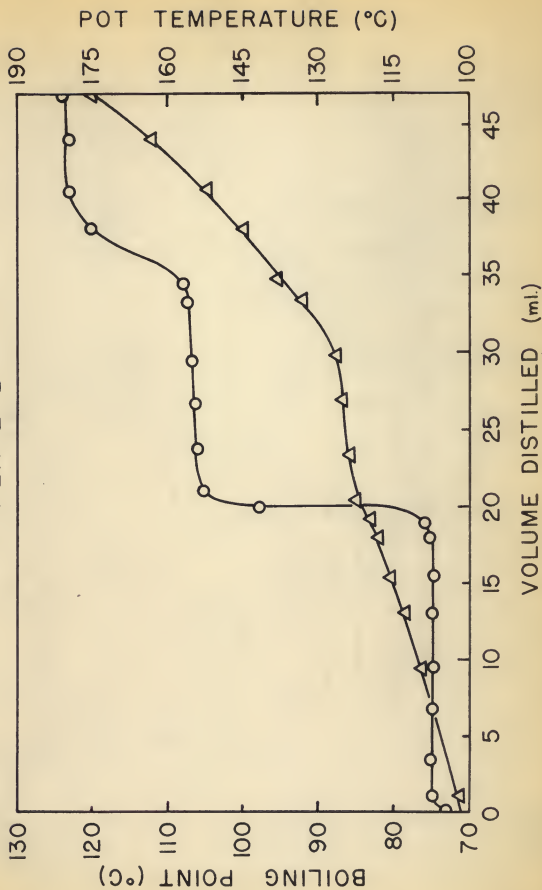
Following the addition of carriers and removal of standards the solution was fractionally distilled. The PCl_3 , POCl_3 , PSCl_3 and decane carriers have the respective boiling points of 75°C , 106°C , 125°C , and 185°C . The majority of the distillations were carried out at atmospheric pressure using a three foot by one inch column packed with glass helices. A typical distillation curve from a solution of these four carriers is shown in Plate I. The decane was not distilled through the long column, instead it was used as a carrier for phosphorus-chlorine compounds having boiling points above 125°C . As Plate I indicates, the maximum pot temperature was about 180°C . The phosphorus activity remaining in the decane was treated in a variety of ways in an effort to establish its identity. These details are discussed later.

Throughout the distillation small fractions (1 to 2 ml) were collected and their P^{32} activity measured. This gave double criteria for the purity of a fraction, i. e. the boiling point and the specific activity. For example the boiling point might remain constant, but the specific activity slowly rises during the collection of the POCl_3 fractions. This would prove that the radioactive material was not POCl_3 because the specific activity would remain constant if the radioactive phosphorus was present as $\text{P}^{32}\text{OCl}_3$. A possible explanation of such a specific activity change could be that a compound in the distillation pot was decomposing giving products which distill at this temperature.

EXPLANATION OF PLATE I

This is the distillation curve from a mixture of 20 ml of PCl_3 , 13.5 ml of POCl_3 and 15.5 ml of PSCl_3 . The circled points show the variation of the boiling point with the number of ml distilled. The triangular points show the variation of the pot temperature with the number of ml distilled.

PLATE I



The data which are shown in Table 1 illustrate the efficiency of the distillation column. The results were obtained using phosphorus trichloride which contained $P^{32}Cl_3$. This material was the PCl_3 fraction from an irradiated sample separated in the previously described manner. The boiling point and specific activity of the fractions were constant, so it was assumed to be chemically pure PCl_3 . Phosphorus oxychloride, phosphorus thiochloride, and reagent grade decane carriers were added to the PCl_3 and the solution distilled in the usual manner. From the counting data of each fraction the specific activity in counts $\text{min}^{-1} \text{ml}^{-1}$ for each carrier was calculated. These results show that good separations of PCl_3 from the other carriers were obtained. The results also indicate that chemically pure PCl_3 does not react with reagent grade decane. However, other data show that the use of purified reagent grade decane is necessary to prevent a reaction between an irradiated sample of PCl_3 and the decane.

Table 1 Efficiency of the distillation column

Carrier	Activity counts $\text{min}^{-1} \text{ml}^{-1}$	Per cent of activity
Phosphorus trichloride	13,485	98
Phosphorus oxychloride	130	1
Phosphorus thiochloride	56	0.4
Decane	66	0.5

In order to eliminate the effects of the high temperatures reached in atmospheric distillations, some distillations at reduced pressures were done. Mixtures of PCl_3 , $POCl_3$, and $PSCl_3$ are difficult to separate at reduced pressure; therefore, only PCl_3 and decane carriers were used. In this technique PCl_3 was removed from the top of the column while decane remained behind. The maximum

pot temperatures were about 60°C .

Counting Technique

Since the chemical species produced by the recoil process will contain P^{32} atoms, a measurement of the quantity of P^{32} present in the various fractions is also a measurement of the quantity of that particular chemical species which is present. Two radioactive elements, P^{32} and S^{35} are present in irradiated samples of PCl_3 . Both P^{32} and S^{35} are beta emitters; their energies are 1.7 Mev and .16 Mev respectively.

In the present approach to the problem, it was necessary to use a counting procedure which would differentiate the radioactivity of P^{32} from that of S^{35} . In addition, a very sensitive technique was needed for measuring the P^{32} activity since the amount of it was low due to the short irradiation periods. The dipping counter arrangement shown in Plate II proved to be highly successful. It has the advantage of having a high geometry (10 per cent); also, low dilution factors can be used for counting sample preparation. The walls of the counter tube are thick enough to absorb all the beta particles from S^{35} as evidenced in the following data. A solution containing 0.465 millicuries of S^{35} was poured into the counting chamber. Only 184 counts min^{-1} above background were recorded and blocking of the scaler was not responsible for the low counting rate. In an irradiation period of 10 minutes 0.2 millicuries of S^{35} are produced. This shows that the S^{35} can not contribute towards the counting rates of the irradiated samples. It should be emphasized that the S^{35} compounds are important, but without complex equipment the analysis of S^{35} in such low quantities is extremely difficult.

Counting samples were prepared from the distillation fractions by pipet-

EXPLANATION OF PLATE II

This is a photograph of the counting apparatus. The tube is a 3/4 inch diameter, glass Tracerlab type TGC 5 Geiger tube, serial 5BT76, with a wall thickness of approximately 30 mg cm⁻². The tube was connected to a Berkeley Decimal Scaler, Model 2000.

CHIEFMAN BOARD

PLATE II



ting aliquots, large enough to give reasonable counting rates, into enough xylene to give a total volume of 15 ml. The aliquots were usually between 0.1 and 2 ml. The xylene solutions were then poured into the counter and the radioactivity measured. Before counting each sample the counter was thoroughly washed and a background reading obtained. For aqueous counting samples water instead of xylene was used as the diluting medium.

RESULTS AND DISCUSSION

Radiation Effect on the Per Cent Retention

The variation of the per cent retention¹ as a function of the neutron dosage was the most important experimental result obtained in this study. Dosage limits from 9.25×10^{11} neutrons cm^{-2} to 1.754×10^{14} neutrons cm^{-2} were investigated. It should be remembered that both the external and internal gamma dosage vary with the neutron dosage.

The data obtained from a typical sample are shown in Table 2. This was an 8.7 ml sample for which the requested neutron dosage was three minutes at a flux of 1×10^{11} neutrons cm^{-1} second⁻¹. The method of calculating the actual neutron dosage is shown in Appendix I. Using this method the actual neutron dose was calculated as 7.42×10^{12} neutrons cm^{-2} . After the addition of carriers and removal of standards, the solution volume was 62.7 ml (18.7 ml PCl_3 , 13.6 ml POCl_3 , 15.4 ml of PSCl_3 , and 15 ml of decane) of which 61.4 ml were recovered as distillate and residue from the distillation; the remaining 1.3 ml were absorbed on the packing of the column. The plot of

¹Per cent retention is defined here as the per cent of total P^{32} activity which is present as P^{32}Cl_3 .

Table 2

Data from a typical sample (sample C)

Fraction	Boiling point	ml distilled	Size of counting aliquot (ml)	Counting rate (counts min ⁻¹)
¹ Standard I-A	---	---	1.00	10,042
Standard I-B	---	---	1.00	9,956
Standard I-C	---	---	1.00	9,647
Standard I-D	---	---	1.00	9,770
Standard II-A	---	---	2.00	7,626
Standard II-B	---	---	2.00	7,593
#1	75°C	2.1	1.00	7,409
#2	76°C	4.2	1.00	7,311
#3	76°C	6.2	1.00	7,198
#4	76°C	8.5	1.00	7,460
#5	76°C	10.6	1.00	7,671
#6	76°C	12.7	1.00	7,770
#7	76°C	14.8	1.00	8,165
#8	76°C	17.0	1.00	9,870
#9	106°C	19.2	1.00	5,894
#10	108°C	22.0	1.00	322
#11	108°C	24.9	2.00	309
#12	108°C	28.1	2.00	184
#13	108°C	30.3	2.00	138
#14	114°C	32.8	2.00	104
#15	122°C	35.5	2.00	148
#16	124°C	37.8	2.00	160
#17	125°C	40.	2.00	137
#18	125°C	42.4	2.00	177
#19	125°C	44.9	2.00	192
² Pot residue above 165°C		44.9-61.4	1.00	2,010

¹The standards refer to those volumes removed prior to the distillation which are used to measure the total P³² activity in the irradiated sample.

²The pot material was further treated before the counting data was taken; therefore, the total activity is not given by direct relationship between counting rate and volume.

these data shown in Plate III, illustrate how the radioactivity was distributed throughout the fractions. It is immediately apparent that most of the radioactivity was in the PCl_3 fractions. Before discussing the distribution of the activity, the method of calculating the per cent of the radioactivity present in the various carriers will be considered.

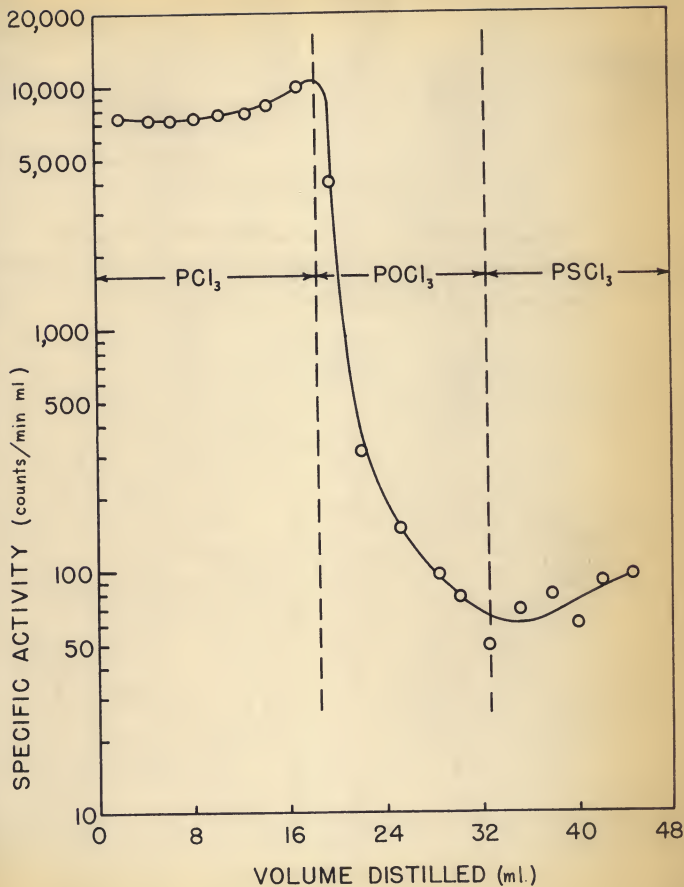
The specific activity of the first few fractions of PCl_3 was constant. Since the boiling point of these fractions was constant and equal to that of PCl_3 , the chemical species containing P^{32} in these fractions must be P^{32}Cl_3 . The peak which is shown in Plate III is an additional radioactivity superimposed upon the radioactivity from P^{32}Cl_3 . Since the radioactivity in the peak is a product from a decomposition reaction occurring in the distillation pot, it was not included in the per cent retention calculations. A discussion of the decomposition reaction is presented later. The per cent retention is calculated by dividing the radioactivity present as P^{32}Cl_3 by the total radioactivity of the sample. The measurement of the total radioactivity has already been discussed. The average counting rate for the PCl_3 fractions was determined from the counting rates of the PCl_3 fractions which did not contain any radioactivity responsible for the peak. In this example they were the first 5 fractions. This average counting rate was used to calculate a specific activity in $\text{counts min}^{-1} \text{ ml}^{-1}$. The specific activity was multiplied by the sum of the volumes of the PCl_3 carrier and the irradiated sample to obtain the total activity present as P^{32}Cl_3 . The method used to calculate the standard deviation in the per cent retention is shown in Appendix II.

The per cent of the total radioactivity present in the peak was estimated by taking a weighted average of the specific activities, subtracting the specific activity of PCl_3 from this and multiplying by the volume of the

EXPLANATION OF PLATE III

This is a plot of the log of the specific activity (counts min^{-1} sec^{-1}) versus the volume of the solution distilled for sample C. The dotted lines show the transitions, from one carrier to another.

PLATE III



liquid in the peak. This calculation is probably correct to within ± 20 per cent.

Since the specific activity never reached a constant value in the POCl_3 fractions, $\text{P}^{32}\text{OCl}_3$, was not present in the irradiated sample. Furthermore the specific activity decreased continuously, indicating that no chemical species were present which would distill in this temperature range. Conn and Hein (17) reported some radioactivity in the POCl_3 carrier and explained it as post irradiation hydrolysis of P^{32}Cl_5 . Since the separation procedures in the present study were superior to those used by Conn and Hein, their results were probably due to incomplete separation of PCl_3 and POCl_3 .

The specific activity does increase in the successive PSCl_3 fractions. This means a chemical species containing P^{32} is present in this carrier. The per cent of the total radioactivity in the PSCl_3 carrier was found by multiplying the average specific activity by the volume of PSCl_3 carrier and then dividing by the fraction of total radioactivity of the sample, which was distilled.

The per cent of the radioactivity in the decane was obtained by multiplying the specific activity of the decane by the proper¹ volume and then dividing by the fraction of the total radioactivity, which was distilled.

The distribution of the radioactivity in the various irradiated samples is shown in Table 3. Column 3 is the calculated irradiation time assuming a flux of 1×10^{11} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ and using the calculated dosage from counting measurements. The flux was not constant for all the irradiation samples; however, the correct dosage relationship was maintained because dos-

¹ The original volume of decane carrier cannot be used because the pot residue was usually treated in various manners before being counted.

Table 3
Tabulation of data from irradiated samples

Sample	Calculated : neutron dosage :	Time : (in seconds) :	Per cent : retention : in PSCl_3 :	Per cent : in decane :	Per cent : in peak :	Per cent : recovery
A	9.25×10^{11}	9.25	67.2 ± 3	1.	19.4	7
B	4.55×10^{12}	45	73.6 ± 3	0.9	12.6	*
C	7.42×10^{12}	74	75.2 ± 2	0.7	14.2	2
D	6.3×10^{12}	63	69.4 ± 3	0.7	14.4	16
E	7.2×10^{12}	72	62.4 ± 2	1.	12.7	17
F	1.51×10^{13}	150	79.7 ± 5	1.	11.4	—
G	6.1×10^{13}	610	94.1 ± 4	0.4	1.04	—
H	1.2×10^{14}	1200	95.4 ± 2	0.8	2.02	—
I	1.75×10^{14}	1750	87.3 ± 3	2.	3.1	—

* This sample contained some activity in the peak, however, the data are too inaccurate to analyze.

Purified decane was used for samples I, D and E.

age is a product of neutron flux and irradiation time, i. e. a decrease in flux results in an increase in irradiation time for the same dosage and vice versa. The last column gives the per cent of the radioactivity recovered from all the carriers compared to the total radioactivity of the sample. The radioactivity which is lost was attributed in part to losses accompanying volume transfers from one container to another. Many such transfers were made in the analysis of each sample. This table summarizes nearly all of the data obtained in this study.

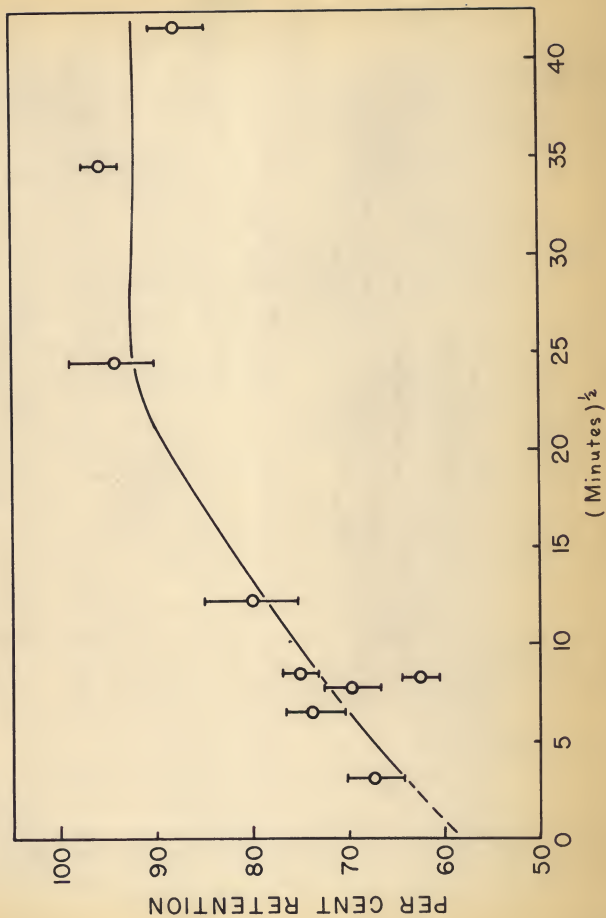
Plate IV is a plot of the per cent retention versus the square root of the irradiation time. The square root time scale was used in order to conveniently graph the results. The standard deviations in the per cent retention determinations are shown by the length of the vertical lines. The probable error in the irradiation time is about ± 5 per cent. This curve shows that the per cent retention or the per cent of P^{32} which is present as $P^{32}Cl_3$ increases with the length of the irradiation time. Expressed another way, it means that the per cent retention is a function of the neutron and gamma dosage. The effect due to the gamma and neutron dosage will be referred to as the radiation effect. After about 625 seconds or a neutron dosage of 6.3×10^{13} neutrons cm^{-2} , the per cent retention reaches a maximum of about 92 per cent. Extrapolation of the curve back to zero time gives between 55 and 60 per cent retention. This indicates that initially between 55 and 60 per cent of the P^{32} atoms were reformed into $P^{32}Cl_3$ while the other 40-45 per cent of the P^{32} atoms are reformed into other chemical species.

The graph in Plate IV indicates that the other chemical species are being converted back to $P^{32}Cl_3$ by the radiation effect. In order to prove this theory, two samples were irradiated in the reactor for short periods of time

EXPLANATION OF PLATE IV

This is a plot of the per cent retention versus the calculated length of irradiation time. The irradiation time was calculated assuming a flux of 1×10^{11} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ and using the dosage obtained from counting measurements. The time was plotted on a square root scale in order to contract the time scale. The dotted line shows the extrapolated region of the graph.

PLATE IV



under as nearly identical conditions as possible. One sample was analyzed immediately, and the other was subjected to an additional gamma dosage of 2.88×10^7 roentgens. The results from these irradiations are shown in Table 4. This was good evidence that the radiation effect was an important

Table 4 Influence of additional gamma dosage on the per cent retention

Sample	Neutron dosage	Additional gamma dosage	Per cent retention	Per cent in decade
J	7.42×10^{12}	none	75 ± 2	14.2
K	6.5×10^{12}	2.9×10^7 r	98 ± 2	.67

factor in the system.

The length of time between irradiation and analysis was a possible variable because sample A was opened and analyzed two days after irradiation while sample B was opened and analyzed six days after irradiation. The possibility of the length of time between irradiation and analysis being a variable was investigated by irradiating two samples with the same neutron dosage and permitting them to stand for different periods of time before beginning the analysis. These were samples D and E, the results of which are shown in Table 3. Sample E was analyzed one day after irradiation and had a 62.4 ± 2 per cent retention. Sample D was analyzed ten days after irradiation and had a 69.4 ± 1 per cent retention. This is an appreciable difference; however, it is small compared to the change in per cent retention produced by the additional gamma dosage. By coincidence sample C also received about the same neutron dosage as samples D and E. Sample C was analyzed one day after irradiation and shows a 75 per cent retention. This demonstrates that the length of time

between irradiation and analysis is a minor variable. With this point established the radiation effect upon the system is proven.

Chemical Species Containing P^{32}

If materials other than PCl_3 are in the irradiated samples, they are present in trace quantities. During irradiation at a neutron flux of 1×10^{11} neutrons $cm^{-2} sec^{-1}$, 2.7×10^9 S^{35} atoms are produced per second. The probability is very small for a reaction between P^{32} atoms and S^{35} atoms which are present in about the same concentration. Clark (11) searched for such doubly labeled molecules as $P^{32}S^{35}Cl_3$ without success in the neutron irradiation of PCl_3 . In view of these results it may be concluded that the principal recombination products of P^{32} are composed of only phosphorus and chlorine atoms.

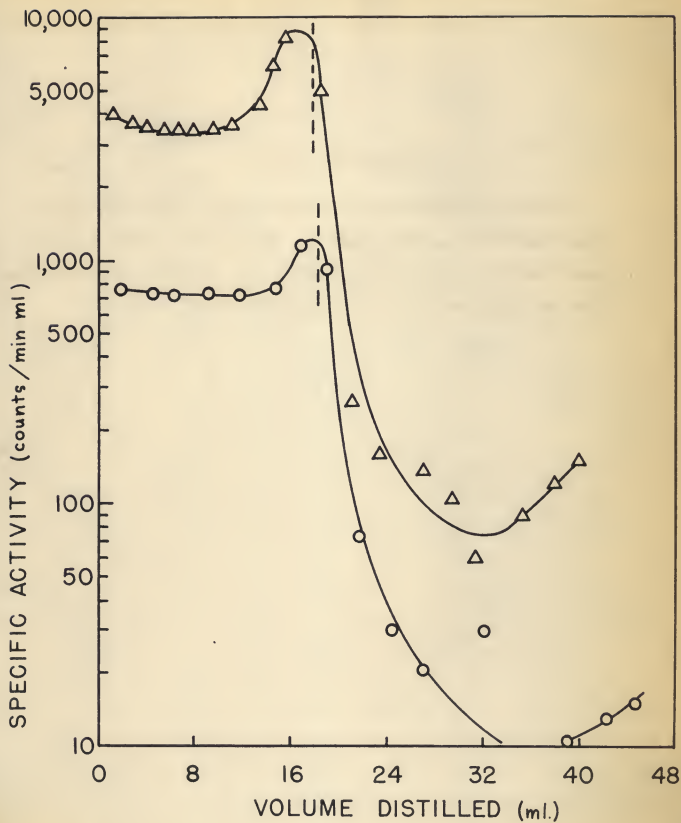
In the previous section it was shown that one of the principal recombination products was $P^{32}Cl_3$ and that no species containing P^{32} were in the $POCl_3$ carrier. In that section the evidence for the presence of a species containing P^{32} in the PCl_3 carrier was also presented. The natural tendency is to attribute this to $P^{32}S^{35}Cl_3$, but in view of Clark's work this seems unlikely. Since that species accounts for only 0.8 - 1.0 per cent of the total activity, it is relatively unimportant and its identification was not attempted.

From Table 3 it is seen that the remainder of the activity is in the decane residue or the peak. The shapes and positions of these peaks for samples A, D, E, and G are shown in Plates V and VI. Results from the plot of sample C are shown in Plate III. Plots of the results from samples F, H, and I have the same pattern as that of sample G. These graphs show that the position of the peaks with respect to the PCl_3 - $POCl_3$ carriers was the same for all samples. In most cases the peak was distributed over a 6 - 8 ml distillation

EXPLANATION OF PLATE V

This is a plot of the log of specific activity (counts min⁻¹ ml⁻¹) versus the volume of solution distilled. The triangular points represent sample D and the circular points sample A. The dotted lines show the transition from PCl_3 carrier to POCl_3 carrier.

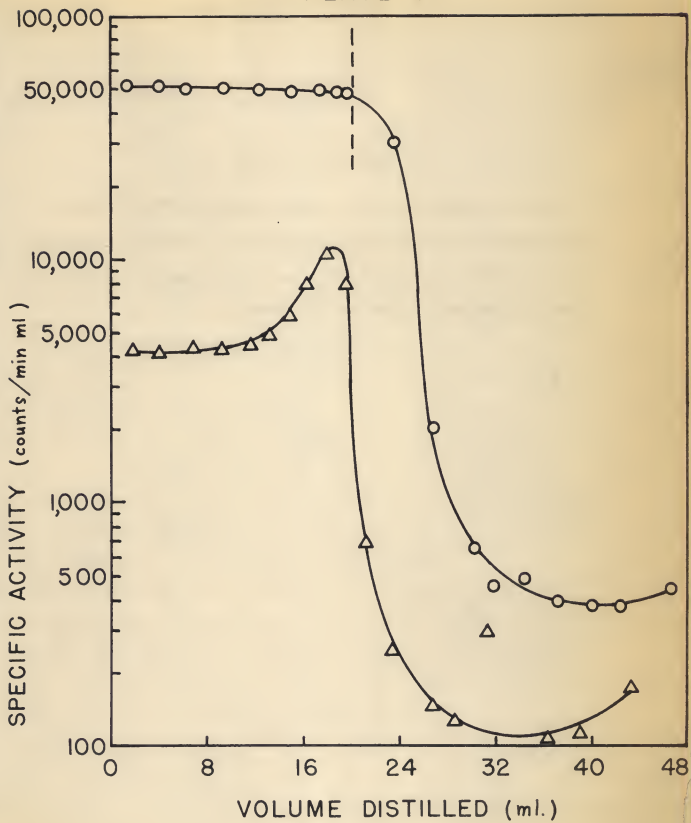
PLATE V



EXPLANATION OF PLATE VI

This is a plot of specific activity (counts $\text{min}^{-1} \text{ml}^{-1}$) versus the volume of solution distilled. Triangular points represent sample E and the circular points represent sample G. The dotted lines show the transition from PCl_3 carrier to POCl_3 carrier.

PLATE VI



cut. For all samples the maximum in the peak corresponds to a pot temperature of $118^{\circ} - 120^{\circ}\text{C}$. It should also be noted from Table 2 that the distillation temperature remained at 70°C through the distillation cut containing the radioactivity responsible for the peak. About 10^{12} P^{32} atoms are present in an irradiated sample of PCl_3 . A species containing P^{32} for which a carrier had not been added should be concentrated in one, or at the most, two fractions by distillation because the number of the species present is so small. Since the radioactivity responsible for the peak was distributed through several fractions, it was concluded that the source of the activity was a decomposition reaction in the pot which yielded a volatile product.

Additional evidence which is shown in Table 5 for a decomposition reaction was obtained from a vacuum distillation separation with part of sample D. In the vacuum distillation the maximum pot temperature was 60°C . The results

Table 5 Vacuum and atmospheric distillation of sample D

Separation	Per cent retention	Per cent in decane	Per cent in peak
Atmospheric dist.	69.4	14.4	16 ± 4
Vacuum dist.	65.5	28.8	0

of the vacuum distillation revealed that no additional radioactivity was present in the fractions which normally gave a peak under atmospheric distillation pressures. It was concluded that the radioactivity in the peak was due to a volatile product formed by a decomposition reaction occurring in the pot at temperatures approaching 120°C .

Results of samples F, G, H and I do not show peaks. These same samples

received the larger neutron dosage and have high per cent retention. This indicated that the chemical species containing P^{32} which decompose in the pot during distillation had been destroyed previous to distillation in the samples receiving a high neutron dosage. Since the per cent retention increases with irradiation time, this chemical species was destroyed by the radiation effect in a manner such that phosphorus trichloride containing P^{32} is produced. Since it is likely that both radiation and thermal decompositions give similar products, the activity responsible for the peak was probably PCl_3 of a high specific activity. In summary the experimental evidence indicated that a chemical species was formed in the recoil process which is decomposed by heat or radiation to form other products, one of which is PCl_3 .

The number of phosphorus-chlorine compounds that have been reported in the literature is limited. PCl_3 and PCl_5 are the common ones. In addition P_2Cl_4 has been reported by Besson and Fournier (3). They listed the boiling point as $180^\circ C$ and freezing point as $-28^\circ C$. Their product decomposed when heated to form PCl_3 and P. It also decomposed upon standing to form the same products. Besson and Fournier's method of preparation consisted of passing H_2 and PCl_3 through a discharge tube with subsequent separation of products by a reduced pressure distillation. Their synthesis is the only reported one for the preparation of P_2Cl_4 . By analogy with the properties observed experimentally in the irradiation studies, it seems likely that P_2Cl_4 is the chemical species which was formed in the recoil process and was decomposed by heat or radiation. The presence of P_2Cl_4 can be used to explain the activity which remained in the pot since P_2Cl_4 should decompose with heat to form non-volatile, elemental phosphorus as one of the products. The presence of P_2Cl_4 was not proven by carrier techniques, but it is the only known compound

which fits the experimental data. In the remainder of the discussion the chemical species which is decomposed by heat or radiation will be referred to as " P_2Cl_4 " with the understanding that if it is not P_2Cl_4 , it is a compound with similar properties.

The relative sizes of the peaks are more difficult to explain than their origin. According to theory, the size should decrease with increasing periods of irradiation. This was not observed due to impurities present in the decane. Since these impurities are removed by concentrated H_2SO_4 , they must be "olefin" or "alcohol like" substances. These impurities do not react with PCl_3 , but they do apparently react with " P_2Cl_4 " to form an unidentified organo-phosphorus compound. This theory is supported by the fact that when unpurified decane was used, much of the P^{32} radioactivity was present as a compound with a boiling point above $180^\circ C$, which was not extracted by H_2O , acid or base and was not chlorinated by PCl_5 to give a water extractable compound. In contrast to this, if purified decane was used, all the pot activity was extractable by water or base. Unpurified decane was used for samples A, B, D, F, G and H while purified decane was used for D, E and I. From a comparison of the results from samples A and D, Plate V, it is seen that the large peaks result from the samples in which the purified decane was used and the smaller peaks from samples in which unpurified decane was used. Comparison of Plates III and VI, samples C and E, show this to be true even for samples that were irradiated for nearly equal periods of time. This behavior can be explained as a reaction between the " P_2Cl_4 " and the impurities in the decane thus inhibiting the decomposition reactions in samples A, B and C. The reaction with the impurities in the decane may cause a slight increase in the per cent retention. At least sample C has a higher per cent retention than samples D or E and yet they are nearly

identical samples except for the use of purified decane for samples D and E. The fact that no peak was present in samples F, G, H and I has already been explained as the radiation decomposition of the " P_2Cl_4 ". Sample I shows that this is true and that the presence of impure decane was not responsible for the absence of the peaks in these longer irradiations.

The P^{32} radioactivity remaining in the decane carrier was completely extracted by water or basic solutions when purified decane was used as the carrier. The high boiling, water soluble compounds responsible for this radioactivity were explained as :

1. Elemental phosphorus which was formed by the decomposition of " P_2Cl_4 " during the atmospheric distillations.
2. Phosphorus acid formed by the hydrolysis of $P^{32}Cl_3$ during the post bombardment handling procedure.

It should be noted that none of these compounds are actually recoil products, but that they are decomposition and hydrolysis products of the original species formed during the recoil process. Ordinary elemental phosphorus, red or white, does not react with water, but any elemental phosphorus in the pot residue is probably present as monatomic phosphorus which should be more susceptible to hydrolysis than the ordinary P_4 units. Carlson and Koski (6) suggested that monatomic phosphorus would disproportionate upon contact with water to give phosphine and phosphorus acid. A similar reaction would seem likely to occur in the pot residues. During the investigation of the radioactivity remaining in the decane it was proven that P^{32} labeled phosphorus sulfides and phosphorus pentachloride were not present. In view of the exchange reaction between PCl_3 and PCl_5 , reported by Becker and Johnson (2), little $P^{32}Cl_5$ would be expected in the irradiated samples even if it was formed in the recoil process.

In summary, the major recoil products containing P^{32} were PCl_3 and a compound resembling P_2Cl_4 . A small per cent of the P^{32} radioactivity was present as an unidentified compound which stayed in the P_3Cl_3 carrier.

Energy Absorbed by an Irradiated Phosphorus Trichloride Sample

The calculation of the energy absorbed per second by a cylindrical sample of phosphorus trichloride while it is in the reactor is shown in Appendix III. The total energy deposited in the sample from all of the energy transfer mechanisms was 1.48×10^{11} Mev per second for an 8 ml sample. This value is probably correct to within a factor of 3. The contribution from the various interactions are tabulated in Table 6. This shows that internal gamma-ray attenuation is responsible for most of the energy deposited in the sample. Further-

Table 6 Energy absorbed by an irradiated sample

Interaction mechanism	Energy deposited per second	Per cent of total
Recoil nuclei from (n, γ) reaction	4.37×10^7 Mev	—
The $Cl(n, p)S^{35}$ reaction	1.69×10^9 Mev	1.35
External γ -ray attenuation	1×10^{10} Mev	6.75
Internal γ -ray attenuation	1.36×10^{11} Mev	91.9
β decay and fast neutron attenuation	negligible	—

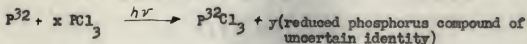
more, the detailed calculations show that the $Cl^{35}(n, \gamma)Cl^{36}$ reaction is responsible for nearly all the energy absorbed from internal gamma-ray attenuation.

It is interesting to note the actual energy deposited to the sample by the

recoiling atoms from the (n,γ) reaction is negligible compared to the total energy absorbed by the sample.

Collins and Calkins (14) and Calkins (5) applied the theory that the same radiolysis products are formed irrespective of the type particles (electrons, gamma rays, proton, etc.) which interact with a system. This theory was assumed true for the present work; that is, each energy transfer mechanism was assumed to give the same radiolysis products. The total energy deposited in the sample and not the energy from each interaction was considered in attempting to explain the radiolysis products of the system.

In an attempt to understand the chemical effects resulting from the attenuation of gamma rays, a 2.3 per cent solution of white phosphorus, containing P^{32} , dissolved in PCl_3 was irradiated with the gamma rays from a Co^{60} source of intensity 2.65×10^6 roentgens hr^{-1} . The solution was subjected to a dosage of 3.6×10^7 roentgens. White phosphorus was used in the experiment because it is soluble in PCl_3 . A portion of the solution was analyzed before irradiation by adding $POCl_3$, $PSCl_3$ and decane carriers and distilling in the usual manner. This separation was done 22 days after the PCl_3 and white phosphorus solution was prepared. About 3 per cent of the P^{32} radioactivity was in the PCl_3 fractions but none of the P^{32} was in the $POCl_3$ or $PSCl_3$ carriers. More work must be done before this exchange can be understood, but it does seem to support the exchange of PCl_3 and elemental phosphorus in carbon disulfide reported by Muxart et al. (39). A similar analysis of the irradiated sample showed that $13\frac{1}{2}$ per cent of the P^{32} radioactivity was in the PCl_3 fractions. The time between the preparation of the mixture and analysis of the irradiated sample was 24 days. Evidently the gamma dosage converted some of the elemental phosphorus into PCl_3 . A generalized reaction may be written:



where x and y are unknown coefficients.

Since the irradiated mixture contained over 95 per cent PCl_3 , most of the energy absorbed by the sample was due to the attenuation of the gamma rays by PCl_3 . Therefore, the energy absorbed was calculated¹ as if the sample contained only PCl_3 . It was found that 2.29×10^{15} Mev were absorbed per gram of sample. The gamma dosage converted 10 per cent or 4.5×10^{19} atoms of the elemental phosphorus into PCl_3 . The G value, i. e. molecules of PCl_3 formed per 100 ev absorbed, for this conversion was thus calculated to be 2.

Recoil Mechanism

The mechanisms taking place in a neutron irradiated PCl_3 sample can be divided into 3 classes; the formation of the recoil products, the interaction of the gamma rays with the PCl_3 , and the effect of the gamma rays upon the recoil products. The recoil mechanism will be discussed first.

Before the recoil mechanism can be understood, the number of phosphorus-chlorine bonds which are broken by the recoiling P^{32} atom must be determined. Maddock and Sutin (36) calculated that over 80 per cent of the arsenic atoms which capture neutrons lose all three phenyl groups when triphenyl arsine is irradiated. They also obtained experimental evidence which supported their calculation. The maximum photon energy emitted by the activated arsenic nucleus is 7.3 Mev, but only 15 per cent of the neutron captures give gamma rays of energy greater than 4.5 Mev. Kinsey et al. (30) show that

¹The method for this calculation is shown in Appendix III under the discussion of the attenuation of external gamma rays.

7.9 Mev is the maximum energy of the gamma rays emitted by phosphorus and that nearly 100 per cent of the neutron captures give a photon of energy equal to or greater than 3.5 Mev. By analogy with the triphenyl arsine irradiations, the recoiling P^{32} atoms should break all three chlorine bonds.

In the present study two samples of $POCl_3$ were irradiated and analyzed in the same manner as the PCl_3 samples. The results of these irradiations are given in Table 7. In spite of the limited number of experiments, the

Table 7 Distribution of radioactivity in neutron irradiated $POCl_3$

Neutron dosage	:	Per cent in PCl_3	:	Per cent in $POCl_3$	:	Per cent in $POCl_3$	:	Per cent in decane
	:		:		:		:	
3.6×10^{13} neutrons cm^{-2}		45		29		4		14
3.6×10^{14} neutrons cm^{-2}		31		44		2		18

trend for increasing percentage of P^{32} as $P^{32}Cl_3$ for decreasing dosage is evident. The $POCl_3$ system appears to show a radiation effect similar to that of the PCl_3 ; that is the $P^{32}Cl_3$ formed in the neutron irradiation of $POCl_3$ is evidently converted back to the parent compound $P^{32}OCl_3$ by a radiation effect. Insufficient data prevents extrapolation back to zero time, but the product distribution of the $POCl_3$ sample subjected to a neutron dosage of 3.6×10^{13} neutrons cm^{-2} indicates that at least two bonds are broken when the phosphorus atom undergoes radiative neutron capture. This conclusion is based on the following argument in which it is assumed that all bonds have equal probability of being broken. If one bond is broken, three $P^{32}Cl_2O$ -fragments for each $P^{32}Cl_3$ -fragment are formed. In the recombination step to form a stable molecule, it is likely that each fragment would merely pick up a chlorine radical since

they should be about three times as abundant as oxygen radicals. Thus the recombination of the fragments from the breaking of one bond should give predominantly $P^{32}OCl_3$. If two bonds are broken, $P^{32}ClO$ and $P^{32}Cl_2$ fragments are formed in equal proportion. These fragments should give about one half $P^{32}OCl_3$ and one half $P^{32}Cl_3$ when they form stable products. If three bonds are broken, three $P^{32}Cl$ fragments for each $P^{32}O$ fragment are formed. It is more difficult to predict the products in this case, but the amount of $P^{32}Cl_3$ should be significantly higher than the amount of $P^{32}OCl_3$. In summary, a qualitative interpretation of the results from two irradiations of $POCl_3$ indicates that at least two and perhaps three bonds are broken after the phosphorus atom captures a neutron.

If the PCl_3 system behaves similarly to $POCl_3$ and triphenyl arsine, the recoiling fragments resulting from the $P^{31}(n,r)P^{32}$ reaction should be either $P-Cl$ or P units. In addition to the fragments having a high kinetic energy, other studies which were discussed in the literature survey indicate that the fragments may be positively charged.

The present study of the PCl_3 system gave indication that the recoil fragment interacted with their surroundings to produce yields between 55 and 60 per cent as $P^{32}Cl_3$, about 30 per cent as a compound which had physical properties similar to $P_2^{32}Cl_4$ ¹, less than 1 per cent as unidentified species which was collected in the $PSCl_3$ carrier, and the remainder as unidentified high boiling species which remained in the decane carriers during distillation of the irradiated sample. These high boiling species may result in part from hydrolysis in post bombardment handling procedure.

¹The superscript 32 signifies that one of the phosphorus atoms in P_2Cl_4 is a P^{32} atom, the other is a P^{31} atom.

Libby (34) developed a formula which can be used to calculate the number of elastic collisions a hot atom must undergo before being thermalized. Using this formula, Conn (15) found that the distance traveled by the P^{32} atom is small since few collisions are needed to thermalize the recoiling particle due to the nearly equal masses of the atoms in PCl_3 . Since the recoil fragment is cooled in a small volume, it will be in a high concentration of radicals. Conn (15) thus concluded that the "billiard ball collision" theory reduced to the "random fragmentation" theory for the PCl_3 system.

The data from the present study supports the "random fragmentation" theory even more strongly. It seems improbable that P^{32} or $P^{32} - Cl$ fragments could form " $P_2^{32}Cl_4$ " in hot collision type reactions. If a high energy P^{32} atom or $P^{32} - Cl$ fragment undergoes a head-on collision with the chlorine atom in a PCl_3 molecule, a P^{32} atom and the PCl_2 radical or the $P^{32}Cl$ and PCl_2 radicals will be near each other after the collision. If the same fragments collide with the phosphorus atom in a PCl_3 molecule, a P^{32} atom and 3 chlorine radicals or the $P^{32}Cl$ radical and 3 chlorine radicals would be near each other after the collision. None of these collisions give radicals in the correct stoichiometric proportions to form $P_2^{32}Cl_4$. Neither are the radicals in sufficient concentration to form a similar polymeric material. Such compounds could be formed in epithermal reactions, but according to Conn (15) the cooled atom is in such a chemical environment that epithermal reactions actually reduce to the "random fragmentation" theory for the PCl_3 system. Applying this theory, the recoil fragment is cooled in a high concentration of chlorine and phosphorus-chlorine radicals. These radicals then combine to form many different products. The "random fragmentation" model would predict the formation of $P^{32}Cl_5$; however, due to the exchange reaction between it and PCl_3 ,

$P^{32}Cl_5$ would be present in small amounts and was not experimentally detected. The fact that " P_2Cl_4 " was observed experimentally strongly supports the "random fragmentation" theory.

Radiation Effects

Experimentally it was observed that gamma dosage induced an exchange between white phosphorus, containing P^{32} , dissolved in PCl_3 to give $P^{32}Cl_3$. It was also observed in the neutron irradiation experiments performed on PCl_3 that gamma dosage converted " $P_2^{32}Cl_4$ " into $P^{32}Cl_3$.

The following mechanism is postulated for the gamma induced exchange reaction. Since elemental phosphorus is present in low concentrations, most of the gamma interactions were with PCl_3 rather than P_4 units. In view of this, it is the author's opinion that a radiolysis product of PCl_3 was the oxidant for converting elemental phosphorus into PCl_3 . Even if some of the gamma rays interacted with the P_4 units, the exchange between the resulting activated P_4 units or elemental phosphorus radicals and PCl_3 should be difficult. When gamma rays are attenuated by PCl_3 it seems likely that chlorine radicals and "chlorine deficient" radicals will be formed. The identity and fate of these "chlorine deficient" radicals are unknown. The chlorine radicals may be scavenged by the elemental phosphorus to give PCl_3 or two chlorine radicals may combine to form Cl_2 , which will quickly react with excess PCl_3 to give PCl_5 . The PCl_5 which is also a good chlorinating agent, could convert the elemental phosphorus to PCl_3 . Since the concentration of elemental phosphorus would be higher than that of chlorine radicals, it seems probable that most of the oxidation was done by chlorine radicals rather than PCl_5 .

According to Chien and Willard (8) a stable radiolysis product must be formed before gamma dosage will effect the products formed by the (n,γ) recoil

process. This is reasonable because an unstable radiolysis product would never build up a sufficient concentration to react with the recoil products. It is quite likely that stable PCl_5 is the oxidizing agent in the neutron irradiated PCl_3 samples. No conclusion regarding the fate or nature of the other radicals formed in conjunction with the chlorine radicals can be made from either the neutron irradiations or the exchange study.

A neutron flux of 1×10^{11} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ produces 10^9 atoms of P^{32} per second in an 8 ml sample of PCl_3 . Calculations show that during irradiation an 8 ml cylindrical sample of PCl_5 absorbs about 1.5×10^{11} Mev of energy per second. Assuming that chlorine radicals are the primary radiolysis products and using the G value of 2 calculated from the measurement of the conversion of P^{32} into P^{32}Cl_3 , at least 6 chlorine radicals were evidently produced for each 100 ev of energy absorbed. Applying this to the 8 ml neutron irradiated sample of PCl_3 shows that about 9×10^{15} chlorine radicals could be formed per second. This is a rough estimate and may be in considerable error, but it does illustrate that the radiolysis products are being formed at a much faster rate than P^{32} atoms. It also gives a rough estimate of the magnitude of the radiation effect.

Plate IV shows that the per cent retention is a function of the length of irradiation time. Since the energy absorbed in the sample is also directly related to the length of irradiation time, the per cent retention is a function of the quantity of energy absorbed in the sample. It is believed that the per cent retention increased because the oxidizing radiolysis products converted " $\text{P}_2^{32}\text{Cl}_4$ " back to P^{32}Cl_3 . Since the per cent retention slowly increases with the length of the irradiation time, the concentration of the oxidizing radiolysis product must slowly increase also. From the chemical nature of the

system it is postulated that the concentration of the oxidizing products reaches a maximum. This is reasonable because the concentration of the corresponding reduced radiolysis products is also increasing with irradiation time. When the concentration of the oxidizing and reducing radiolysis products become sufficiently large, they may react with each other giving PCl_3 , the parent compound, as fast as they are being formed from it.

The radiation effect can be used to explain why Conn and Hein (17) obtained the same per cent retention from irradiations of PCl_3 in both the liquid and gaseous state. Conn and Hein irradiated all their samples for 18 hours or longer. Even if a variety of recoil products were formed, they were converted back to P^{32}Cl_3 during these long irradiation periods.

SUMMARY

It was experimentally observed that neutron irradiation of PCl_3 produced two major recoil products containing P^{32} : PCl_3 and a compound having properties resembling those reported for P_2Cl_4 . Extrapolation of the data indicated that between 55 and 60 per cent of the P^{32} initially recombined as PCl_3 and about 30 per cent as a compound resembling P_2Cl_4 . These data support the "random fragmentation" theory for the recombination process in the PCl_3 system.

It was also observed that the per cent of P^{32} present as PCl_3 increased with neutron or gamma dosage to a maximum of about 92 per cent. The compound resembling P_2Cl_4 was not present in the samples which had 92 per cent of the P^{32} in the form of PCl_3 because the large gamma dosage converted the compound resembling P_2Cl_4 back to PCl_3 . It was postulated that PCl_5 molecules were produced by the radiolysis of PCl_3 and reacted with the compound resembling P_2Cl_4 to yield PCl_3 .

An approximate calculation of the total energy deposited in the PCl_3 sample during irradiation was made. It was found that the attenuation of the internally generated gamma rays was the greatest single contribution to the energy deposited in the sample. It was also learned that the absorption of this energy produced radiolysis products which were present in a much higher concentration than the recoil products from the (n, γ) reactions.

Results of a gamma induced exchange between white phosphorus dissolved in PCl_3 showed that oxidizing radiolysis products were formed which could convert elemental phosphorus into PCl_3 . It was postulated that either chlorine radicals or PCl_5 molecules were the oxidizing radiolysis products produced by the attenuation of the gamma rays.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. R. E. Hein and Dr. H. C. Moser for their guidance, encouragement and helpful suggestions during the course of the research.

He is very grateful to Mr. T. J. Clark and Mr. L. F. Grantham for their laboratory assistance and many helpful discussions. The author is also grateful to Dr. R. D. Dragsdorf for his assistance in the calculation of the energy deposited by the internally generated gamma rays and to Dr. I. C. Hisatsune for his helpful suggestions.

Acknowledgment is made to the Atomic Energy Commission for the provision of funds which made the research possible.

The author wishes to thank his sister, Mrs. Merle Evers, for the preparation of the manuscript.

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 97. 2008-2009
 98. 2009-2010
 99. 2010-2011
 100. 2011-2012

APPENDICES

APPENDIX I

Calculation of the Neutron Dosage Received by the PCl_3 Samples

The number of P^{32} atoms, N , formed from No P^{31} atoms when the latter are irradiated with thermal neutrons in a constant flux, ϕ neutrons $\text{cm}^{-2} \text{sec}^{-1}$, is given by the equation:

$$N = \frac{\text{No} \sigma \phi}{\lambda} [1 - e^{-\lambda t}]$$

σ is the thermal neutron capture cross section for P^{31} atoms, $0.19 \times 10^{-24} \text{ cm}^2$, λ is the decay constant for P^{32} , $5.45 \times 10^{-7} \text{ sec}^{-1}$; and t is the period of irradiation. The thermal neutron capture cross section reported by Hughes (28) was used in the present study. The derivation of this equation can be found in nearly all radiochemistry books. If $e^{-\lambda t}$ is expanded in a power series, it is seen that for irradiation periods of less than 10^5 seconds, which includes all of the irradiations in the present study, the terms of higher order than λt can be ignored. Thus the P^{32} radioactivity, λN , in disintegrations sec^{-1} , is closely approximated by the expression $N = \text{No} \sigma \phi t$.

The calculations of the total neutron dosage were made on the basis of a 1ml sample. From the experimental measurements of the radioactivity per ml based on the volumes of the irradiated samples the dosages, ϕt , were calculated. It is

estimated that the deviation of these determinations is about ± 5 per cent due to the inaccuracy of the sample volume measurements. The absolute error in these determinations may be in error by ± 15 per cent, due to the uncertainty in the thermal neutron capture cross section for phosphorus and to the uncertainty in the geometry of the counting device.

Representative Calculation of Neutron Dosage

1. Volume of PCl_3 : 8.7 ml.
2. Counting rate of total sample (obtained from counting rates of standards): 278,700 counts min.⁻¹
3. Total activity present (calculated from 10 per cent geometry of the counting apparatus): 2.782×10^6 disintegrations min.⁻¹
4. The specific activity: 5.33×10^3 disintegrations sec⁻¹ ml⁻¹.
5. Substituting 5.33×10^3 disintegrations sec⁻¹ ml⁻¹ for λN , 6.89×10^{21} P³¹ atoms ml⁻¹ for No, 5.45×10^{-7} sec⁻¹ for λ , and 0.19×10^{-24} cm² for σ into the equation: $\phi t = \lambda N / \lambda \sigma \lambda$ and solving for the dosage, ϕt , gives 7.42×10^{12} neutrons cm⁻².

APPENDIX II

Calculation of Standard Deviation in the Per Cent P^{32}
Retained as $P^{32}Cl_3$

The standard deviation in the per cent retention was calculated using the usual statistical equations. These equations are shown in Friedlander and Kennedy (21). There are two sources of error; the random nature of the disintegration of radioactive nuclei and the error in the preparation of counting samples. A sufficient number of counts was observed for each sample so that the standard deviation of the counting rate was negligible. Therefore, the major error was in the preparation of counting samples.

The standard deviation was calculated using the following three steps:

1. From the counting rates of the individual samples the average counting rate per ml of PCl_3 was found. The standard deviation, σ_1 , was calculated using the equation:

$$\sigma_1 = \left[\sum_{i=1}^n (X_i - \bar{X})^2 / n \right]^{1/2}$$
 where X_i is the counting rate of each individual sample and n is the number of counting samples. This was converted to the total radioactivity present as PCl_3 by multiplying by the volume of PCl_3 . The total counts min^{-1} is given by the relationship:

$$(\text{ml} PCl_3) [X \pm \sigma_1] = R_1 \pm \sigma_1'$$
2. The counting samples from the standards were treated in the same manner. This gives the total radioactivity present in the sample as $R_2 \pm \sigma_2'$.

3. The standard deviation in the per cent retention was calculated from the following formula:

$$\nabla_Q = Q \sqrt{\left(\frac{\nabla_1'}{R_1}\right)^2 + \left(\frac{\nabla_2'}{R_2}\right)^2}$$

where Q is the per cent retention, R_1 divided by R_2 .

APPENDIX III

Calculation of the Total Energy Absorbed by a Phosphorus Trichloride Sample

A cylinder of 8ml volume with a height of 4.0 cm and radius of .8 cm was used as the hypothetical sample for this calculation. Such a sample is representative of the average shape and size of the samples that were irradiated. A neutron flux of 1×10^{11} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ and gamma intensity of 5.6×10^4 roentgens hr^{-1} were used in the calculation. The calculation was made on the basis of the energy deposited per second, and each energy transfer mechanism was treated independently. The sum of the energy absorbed from all the mechanisms is probably correct to within a factor of three.

I. The energy deposited by the recoiling atoms from the (n,r) reactions.

The energy deposited by each reaction was found by multiplying the number of atoms formed per second times the recoil energy of each atom. The number of atoms formed per second was calculated from the formula: $N = N_0 \sigma \phi$ where N_0 is the number of atoms present capable of undergoing the particular reaction, σ is the thermal neutron capture cross section which was obtained from Hughes and Harvey (28), and ϕ is the neutron flux. It is not possible to calculate the recoil energy accurately for multiple gamma-ray emission. An estimate was obtained by using the equation; $E_{\text{recoil}} = 536 E_r / M \text{ ev}$ where E_r is the average gamma-ray energy and M is the mass

of the recoiling atom in atomic mass units. E_r was determined by dividing the Q value (difference in rest mass of the reactants and products) by the average number of gamma rays released per neutron capture. The mass of the atoms were obtained from Kinsman (31). The necessary constants for these calculations are given in Table 8.

Table 8 Constants for the (n, γ) reactions

Reaction	Number of parent atoms	Absorption cross sections	Q-values
$P^{31}(n,\gamma)P^{32}$	5.5×10^{22}	$0.19 \pm 0.03 \times 10^{-24}$	7.90 Mev
$Cl^{35}(n,\gamma)Cl^{36}$	1.245×10^{23}	$30 \pm 20 \times 10^{-24}$	8.56 Mev
$Cl^{37}(n,\gamma)Cl^{38}$	4.08×10^{22}	$0.56 \pm 0.12 \times 10^{-24}$	6.11 Mev

A. $P^{31}(n,\gamma)P^{32}$ reaction

Muehlhause (38) found an average of 2.5 gamma rays emitted per neutron capture for light elements; therefore, E_r equals 3.17 Mev. Multiplying the number of P^{32} atoms produced per second, 1.02×10^9 , times the expression $(3.17)^2 \cdot 536/32$, gives 1.77×10^5 Mev as the energy deposited per second.

B. $Cl^{35}(n,\gamma)Cl^{36}$ reaction

3.7×10^{11} Cl^{36} atoms are produced per second. Muehlhause (38) obtained an average of 3.1 gamma rays per neutron capture for this reaction. This gives 2.77 Mev as the average gamma-ray energy. From these values the energy deposited per second was calculated as 4.5×10^7 Mev.

C. $\text{Cl}^{37}(\text{n},\gamma)\text{Cl}^{38}$ reaction

2.29×10^9 Cl^{38} atoms are produced per second. Using 2.5 gamma rays as the average number emitted per capture, the average gamma-ray energy is 2.44 Mev. These values give 1.9×10^5 Mev as the energy deposited per second.

II. The energy deposited by the $\text{Cl}^{35}(\text{n},\text{p})\text{S}^{35}$ reaction

In this reaction both the S^{35} and the proton deposit all their kinetic energy in the sample. The sum of their kinetic energies is the Q of the reaction. Therefore, the energy deposited by this reaction was calculated by multiplying the number of reactions per second times the Q value (0.617 Mev). The thermal neutron cross section is 0.22107×10^{-24} cm^2 . Using this value and the number of Cl^{35} atoms present, it was found that 2.73×10^9 atoms of S^{35} were produced per second. Thus the above reaction deposits 1.69×10^9 Mev per second in the sample.

III. Energy deposited from external gamma-ray attenuation

According to Calkins (5) the energy deposited from the attenuation of external gamma rays can be approximated by the formula, $E_g = E_r \phi \mu/p$. E_g is the energy absorbed per gram of sample, E_r is the energy of the gamma ray, ϕ is the gamma flux, and μ/p is the energy absorption cross section (cm^2/gm) for the absorbing material. This formula is applicable whenever samples are small enough that they do not remove an appreciable number of photons from the flux. Since our samples meet this requirement, the equation was used.

According to Collins and Calkins (14) the average energy

of the gamma rays in the reactor is estimated as 1 Mev, thus giving a gamma flux of 2.95×10^{10} gamma rays $\text{cm}^{-2} \text{sec}^{-1}$ corresponding to the intensity¹ of 5.6×10^4 roentgens hr^{-1} . The energy absorption cross section for PCl_3 should be a weighted average of the absorption cross sections for both phosphorus and chlorine. Energy absorption cross sections for phosphorus and chlorine have not been reported, but Rockwell (43) lists the absorption cross section of aluminum as a function of the gamma-ray energy. Since the cross section varies as Z/A where Z is the atomic number and A is the atomic weight, the cross section for P, Cl, and Al should be nearly the same. In view of this the energy absorption cross section for aluminum was used for that of PCl_3 in the calculation of both the attenuation of external and internal gamma rays. The energy absorption cross section of aluminum for 1 Mev gamma rays is $0.027 \text{ cm}^2/\text{gm}$. Substituting these values into the above equation gives 1.01×10^{10} Mev as the energy deposited in the sample per second.

IV. Energy deposited from internally generated gamma rays

In order to accurately calculate the energy deposited in the sample by the internally generated gamma rays, the average distance from all points inside the cylinder to the surface of the cylinder must be known. An exact calculation of this quan-

¹The gamma intensity was converted to gamma-ray flux using the conversion factor, 5.27×10^5 gamma rays $\text{cm}^{-2} \text{sec}^{-1} = \text{roentgen hr}^{-1}$.

tity proved to be too difficult so an approximation was used. In the approximation all of the PCl_3 was placed in two planes within the sample. Each of these planes, which are shown in Figure 1, Plate VII, contain one-half of the sample. In addition the gamma rays are restricted to paths perpendicular to the planes. From Figure 2, Plate VII, it is seen that the average vertical distance, $\bar{x}$, is 2 cm while the average horizontal distance, $\bar{y}$, is .628 cm. This approximation method breaks the actual path lengths into horizontal and vertical components, then an approximate average value for these components was found.

There are four internal gamma sources; the $\text{P}^{31}(\text{n},\gamma)\text{P}^{32}$ reaction, the $\text{Cl}^{35}(\text{n},\gamma)\text{Cl}^{36}$ reaction, the $\text{Cl}^{37}(\text{n},\gamma)\text{Cl}^{38}$ reaction, and the gamma rays from the radioactive decay of Cl^{38} . The number of gamma rays from the first three sources was obtained by multiplying the number of reactions per second times the average number of gamma rays released per neutron capture for that reaction.

Cl^{38} has a half-life of 38 minutes and consequently does not deposit its energy as quickly as the other reactions. The number of Cl^{38} atoms which decay per second at any time during the irradiation is given by the formula:

$$\lambda N = N_0 \sigma \phi [1 - e^{-\lambda t}]$$

where λN is the number of decays, N_0 is the number of Cl^{37} atoms in the sample, σ is the thermal neutron absorption cross

section for Cl^{37} , ϕ is the thermal neutron flux, λ is the decay constant for Cl^{38} , and t is the length of irradiation time. The number of gamma rays produced by this source at any given time can be calculated from this formula and information from the decay scheme for Cl^{38} which is shown in Fig. 3, Plate VII. The longest irradiation period in this study was 1750 seconds. The data for the energy deposited in the one-thousand seven-hundred and fifth second are shown in Table 9. This is the maximum energy deposited per second from the decay of Cl^{38} for any of the irradiated samples. Similar calculations show that in the five-hundredth second about one-third as much energy was deposited. Even the maximum energy deposited per second from the decay of Cl^{38} atoms is negligible compared to the total energy absorbed by the sample.

The energy deposited in the sample was calculated for each source using the formula:

$$E_{\text{abs}} = \phi E_r [1 - e^{-\mu/\rho \cdot \rho \cdot \bar{x}}] + \phi E_r [1 - e^{-\mu/\rho \cdot \rho \cdot \bar{y}}]$$

where μ/ρ is the energy absorption coefficients of PCl_3 for the gamma ray of energy: E_r , and $\bar{x}$ and $\bar{y}$ are the average vertical and horizontal distances respectively, ρ is the density of PCl_3 and ϕ is one-half the number of gamma rays emitted per second from that particular source. This equation is a modification of the usual formula found in textbooks for X and gamma ray attenuation. The necessary data and the results are shown in Table 9.

Table 9 Energy Deposited from Internal gamma rays

Source	Q value (Mev)	Ave. energy of gamma rays	Gamma rays per second	μ/ρ .cm ² /gm.	Energy abs.(Mev)
$P^{32}(n,r)P^{32}$	7.94	3.17	2.55×10^9	.0208	3.3×10^8
$Cl^{35}(n,r)Cl^{36}$	8.56	2.77	1.156×10^{12}	.0215	1.35×10^{11}
$Cl^{37}(n,r)Cl^{38}$	6.11	2.44	5.74×10^9	.022	6.2×10^8
Cl^{38} decay					
η		2.15	4.51×10^8	.023	6.7×10^7
τ_2		1.6	2.9×10^9	.025	
Total					1.36×10^{11}

In addition to the assumptions listed above there is another inherent assumption in the calculations for the energy deposited from both the external and internal gamma-ray attenuation. These calculations assume that all the high energy electrons from the Compton by processes are absorbed in the sample. For high energy gamma rays the principal means of attenuation are Compton collisions in which about one-half the photon energy is transferred to the electron. The range of a 1 Mev electron in Al is 0.16 cm. Therefore, Compton collisions near the surface of the cylinder may give electrons which escape from the samples. There is a compensating factor; the attenuation of gamma rays by the quartz container will create some high energy electrons which will enter the PCl_3 . Considering the magnitude of the other assumptions, no correction can be made due to these effects.

Conn (16) calculated more rigorously the energy absorbed by a spherical sample of PCl_3 . The relative contributions from the different interactions are about the same for both the spherical sample and the cylindrical sample. In addition, Conn

calculated the energy absorbed from fast neutron attenuation and β^- decay of P^{32} , Cl^{38} , and Cl^{36} . The energies absorbed from both processes were negligible in comparison to the total energy absorbed. In view of Conn's results the energy absorbed from these last two processes was ignored in the calculations for the cylindrical sample.

The values obtained for the energy deposited in the sample by the various processes are tabulated below.

I.	Recoil atoms from (n, γ) reactions	$= 4.34 \times 10^7$ Mev
II.	$Cl^{35}(n,p)S^{35}$ reaction	1.69×10^9 Mev
III.	External gamma-ray attenuation	1.01×10^{10} Mev
IV.	Internal gamma-ray attenuation	1.36×10^{11} Mev
Total		$= 1.48 \times 10^{11}$ Mev

EXPLANATION OF PLATE VII

- Fig. 1. Diagram of the two planes (A and B) within the cylinder in which the PCl_3 sample is assumed to be located for the calculation of the attenuation of internal gamma rays.
- Fig. 2. Calculation of the average perpendicular distance from plane B to the surface of the cylinder, this average distance is calculated using equal increments along the diameter.
- Fig. 3. Diagram of the decay scheme for the Cl^{38} nucleus.

PLATE VII

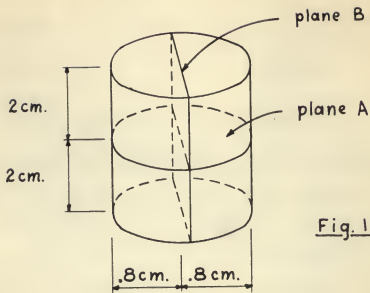


Fig. 1

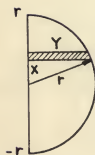


Fig. 2

$$\bar{X} = \frac{h}{2} = 2 \text{ cm.}$$

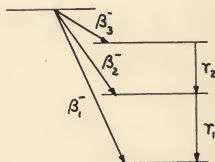
$$\bar{Y} = \frac{\int_{-r}^r (r^2 - x^2)^{\frac{1}{2}} dx}{\int_{-r}^r dx} = \frac{\pi r}{4}$$

$$= .628 \text{ cm.}$$

4.81 Mev

3.75 Mev

2.15 Mev



$$\beta_1^- = 53\%$$

$$\beta_2^- = 16\%$$

$$\beta_3^- = 31\%$$

$$r_1 (2.15 \text{ Mev}) = 47\%$$

$$r_2 (1.6 \text{ Mev}) = 31\%$$

Fig. 3

THE CHEMICAL EFFECTS OF NEUTRON AND
GAMMA IRRADIATION OF PHOSPHORUS
TRICHLORIDE

by

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B. S., Kansas State College of Agriculture
and Applied Science, 1956

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1958

The chemical effects accompanying the $P^{31}(n,\gamma)P^{32}$ nuclear reaction were studied by irradiating samples of PCl_3 with thermal neutrons. Since P^{32} is radioactive, the chemical species containing the P^{32} atoms could be detected by counting techniques.

In addition to the $P^{31}(n,\gamma)P^{32}$ nuclear reaction the following nuclear reactions also occur when PCl_3 is irradiated: $Cl^{35}(n,p)S^{35}$, $Cl^{35}(n,\gamma)Cl^{36}$ and $Cl^{37}(n,\gamma)Cl^{38}$. Energy is deposited in the irradiated PCl_3 sample from the attenuation of these internally generated gamma rays, attenuation of the gamma rays present in the nuclear reactor, and the absorption of the kinetic energy from the recoil products. Calculations showed that the attenuation of the internally generated gamma rays was the largest single contribution to the energy absorbed during irradiation. The absorption of this energy produces radiolysis products which are present in a higher concentration than the recoil products from the (n,γ) reactions.

These radiolysis products may react with the recoil products, thus destroying the initial species formed following the $P^{31}(n,\gamma)P^{32}$ reaction. This possibility was investigated by irradiating PCl_3 samples, which had been purified by several successive fractional distillations, for various lengths of time in the Oak Ridge X-10 graphite reactor. The irradiated samples were returned to Kansas State College for analysis. PCl_3 , $POCl_3$, $PSCl_3$ and decane carriers were added to the irradiated samples and the solutions were fractionally distilled. Small fractions, between one and two ml, were collected throughout the distillations, and their P^{32} radioactivity was measured with a dipping counter tube. The walls of the counter tube were thick enough so that only the P^{32} radioactivity was measured.

The data showed that two major recoil products were formed by neutron irradiation of PCl_3 : $P^{32}Cl_3$ and a compound having properties resembling

those reported for P_2Cl_4 . Extrapolation of the data indicated that in the recombination process between 55 and 60 per cent of the P^{32} was present as PCl_3 and about 30 per cent as a compound resembling P_2Cl_4 . The remainder of the P^{32} radioactivity was present as unidentified species. These data support the "random fragmentation" theory for the recombination process in the PCl_3 system.

It was observed that the per cent of P^{32} present as $P^{32}Cl_3$ increased with the neutron and gamma dosage to a maximum of about 92 per cent. This maximum occurred after an irradiation period of about 625 seconds at a neutron flux of 1×10^{11} neutrons $cm^{-2} sec^{-1}$ and a gamma intensity of 5.6×10^4 roentgens hr^{-1} . This effect gives indication that radiolysis products react with the recombination product resembling P_2Cl_4 to convert it to PCl_3 .

Results of a gamma-ray induced exchange of P^{32} between dissolved white phosphorus and PCl_3 showed that oxidizing species are formed by the radiolysis of PCl_3 which are capable of converting elemental phosphorus into PCl_3 . For this exchange it was postulated that either chlorine radicals or PCl_5 molecules were the oxidizing radiolysis products. In the neutron irradiations it was postulated that PCl_5 molecules were the oxidizing radiolysis products.